

Observation of two distinct d_{xz}/d_{yz} band splittings in FeSe

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We report the temperature evolution of the detailed electronic band structure in FeSe single-crystals measured by angle-resolved photoemission spectroscopy (ARPES), including the degeneracy removal of the d_{xz} and d_{yz} orbitals at the Γ/Z and M points, and the orbital-selective hybridization between the d_{xy} and $d_{xz/yz}$ orbitals. The temperature dependences of the splittings at the Γ/Z and M points are different, indicating that they are controlled by different order parameters. The splitting at the M point is closely related to the structural transition and is attributed to orbital ordering defined on Fe-Fe bonds with a d -wave form in the reciprocal space that breaks the rotational symmetry. In contrast, the band splitting at the Γ points remains at temperature far above the structural transition. Although the origin of this latter splitting remains unclear, our experimental results exclude the previously proposed ferro-orbital ordering scenario.

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Several experimental studies report the breakdown of the rotational symmetry in parent and underdoped compounds of Fe-based superconductors (FeSCs) [1–4] that is commonly referred to as nematicity. Its origin is highly debated since both magnetic [5–8] and orbital [9–12] fluctuations or orderings can lead to nematicity. Although strong support is given to magnetic-driven nematicity in iron-pnictides [13] where the orthorhombic lattice distortion is always accompanied by a collinear magnetic order at a temperature equal to or below the lattice transition temperature, this mechanism is questioned in FeSe, which exhibits an orthorhombic lattice distortion below the distortion transition temperature $T_s \sim 90$ K without any trace of magnetic order. As a direct signature of the electronic anisotropy between the x and y directions in the nematic state, previous angle-resolved photoemission spectroscopy (ARPES) studies [14–16] revealed a splitting between the otherwise degenerate Fe $3d_{xz}$ and Fe $3d_{yz}$ orbitals at the M point of the Brillouin zone (BZ). This splitting is widely believed to be a key evidence for ferro-orbital ordering in the nematic phase [9, 17–19].

In this letter we report the existence of two distinct splittings between the d_{xz}/d_{yz} bands of FeSe single-crystals near the Fermi level (E_F). We show that a first splitting decreases with temperature increasing, and disappears at about 100 - 120 K, which is slightly higher than T_s , suggesting that it is caused by short-range orbital order or fluctuations related to the structural transition. This splitting has a d -wave form breaking rotational symmetry [20] that is the largest at the M point and that is inconsistent with ferro-orbital ordering. In addition, we observe a splitting at the Γ point that is rather

insensitive to temperature up to 150 K, way above T_s . Due to the strong orbital-selectivity of the hybridization between the d_{xy} band and the d_{xz} and d_{yz} orbitals, we conclude that the splitting at the Γ point is not simply due to spin-orbit coupling (SOC).

High-quality single-crystals of β -FeSe were grown by the KCl/AlCl₃ chemical vapor transport method [21]. The T_c was determined to be 9 K from magnetization measurements and a structural transition is observed around 90 K. ARPES measurements were performed at the Dreamline beamline of the Shanghai Synchrotron Radiation Facility (SSRF) using a VG-Scienta D80 electron analyzer, and at the Institute of Physics, Chinese Academy of Sciences, using a R4000 analyzer and a helium discharge lamp. The angular resolution was set to 0.2°. Clean surfaces for the ARPES measurements were obtained by cleaving the samples *in situ* in a working vacuum better than 5×10^{-11} Torr. In the text, we label the momentum values with respect to the 1 Fe/unit cell BZ.

We show in Fig. 1 the electronic band structure of FeSe, below the structural transition. The Fermi surface (FS) (Fig. 1(a)) is formed by one hole pocket centered at Z and two electron pockets centered at A. Based on local density approximation (LDA) calculations (Supp. Part I), we attribute the two elliptical electron pockets at A to $d_{xz/yz}$ bands in different twin domains, while the d_{xy} electron pocket is not observed. A schematic representation of the FSs ($T > T_s$) and their areas are shown in Supp. Part III. As shown in Fig. 1(b), the k_z dispersion along Γ -Z is non-negligible, in agreement with a previous report [22]. The Fermi wave vector (k_F) near

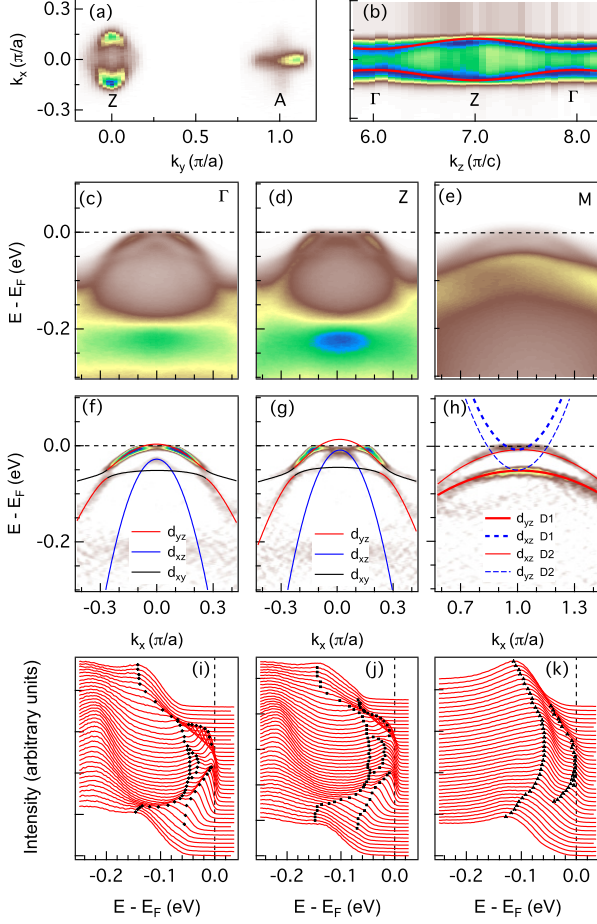


FIG. 1. (a) FS mapping along the Z(0, 0, π)-A(0, π , π) direction, recorded with unpolarized He I α photons. (b) FS mapping along the Γ (0, 0, 0) - Z direction obtained in the σ geometry. The red solid lines indicate the k_z dispersion. (c - e) Band structure at Γ , Z and M (0, π , 0) along Γ -M or Z-A with $T < T_s$, recorded in the σ geometry. (f - h) 2D curvature of (c - e). The red, blue and black lines indicate the dispersions of the d_{yz} , d_{xz} and d_{xy} orbitals, respectively. The thick and thin lines in (h) correspond to 2 different domains. (i - k) EDC plots of (c - e). The black dots indicate the EDC peaks.

the Γ point is $\sim 0.07\pi/a$, while it is $\sim 0.14\pi/a$ at the Z point. The small k_F can be clearly resolved from the cut at Γ displayed in Figs. 1(c), 1(f) and 1(i). Besides the d_{yz} band, we also resolve a steep d_{xz} and a flat d_{xy} bands below E_F . Interestingly, the top of the d_{xz} and d_{yz} bands do to coincide, in contrast to LDA calculations but in agreement with a previous ARPES report [16]. From the energy distribution curves (EDCs) and curvature intensity plots [23], we estimate that the splittings at Γ is about 30 meV at $T \sim 20$ K. As shown in Fig. 1(f), we notice that there is a large hybridization gap between the d_{yz} and d_{xy} bands near Γ but little hybridization or none

between the d_{xy} and d_{xz} bands.

The band structure at Z (Figs. 1(d), 1(g) and 1(j)) is very similar, except for a relative shift along the energy direction. In particular, a splitting of about 30 meV is observed at Z between the d_{xz} and d_{yz} bands, and an hybridization gap is found between the d_{xy} and d_{yz} bands, but not between the d_{xy} and d_{xz} . In Figs. 1(e), 1(h) and 1(k), we show the band structure at M. We distinguish two hole-like bands associated with the d_{yz} bands from different twin domains. Because of a lack of coherence, the d_{xy} electron and hole bands at M are not observed. Our data indicate that the splitting at M is about 50 meV at $T \sim 50$ K, which is quite different from the prediction of onsite interactions.

To fully understand the splittings and check if they are related, we performed temperature-dependent experiments. The temperature evolution of the d_{xz}/d_{yz} splittings at high-symmetry points is illustrated in Fig. 2. Except for thermal broadening, the intensity plots show that the band dispersions around Γ barely change with temperature and that the separation between the d_{xz} and d_{yz} bands is nearly temperature independent. In other words, the d_{xz}/d_{yz} splitting at Γ is almost not changed within the temperature range studied, and the hybridization gap between the d_{xy} band and the d_{yz} band persists at high temperature, whereas no hybridization is found between the d_{xy} band and the d_{xz} band, indicating that none of these phenomena is directly related to the structural transition. Our conclusion on the splitting at Γ is reinforced by the comparison of the EDCs at the Γ point, displayed in Fig. 2 (u), and at the Z point (see Supp. FigS2).

Unlike our observation at Γ /Z, the band splitting at M varies strongly with temperature. The two sets of bands from different domains gradually merge with increasing temperature. At $T = 120$ K, we only see one set of band structure, which implies the disappearance of the domain structure, in agreement with previous results [14–16]. The evolution of the EDCs with temperature at M is shown in Fig. 2 (v). The dashed lines mark the two sets of band tops/bottoms merging at $T = 120$ K.

Fig. 3(a) compares the temperature dependence of the different splittings and Fig. 3(b) gives a schematic representation of the experimental splittings and hybridizations observed below and above T_s . The splittings at Γ and Z have the same amplitude, which varies very slowly with temperature, even across the structural transition. In sharp contrast, the splitting at the M point is nearly twice that at the Γ point at low temperature, but it decreases with temperature and vanishes at 100 - 120 K. We conclude that we must introduce two parameters to explain the data. The splitting at Γ /Z is temperature independent and affects only the BZ area around Γ and Z, while the parameter inducing the splitting at M only affects the M point and is related to structural transition. Since it does not affect the splitting at the BZ center,

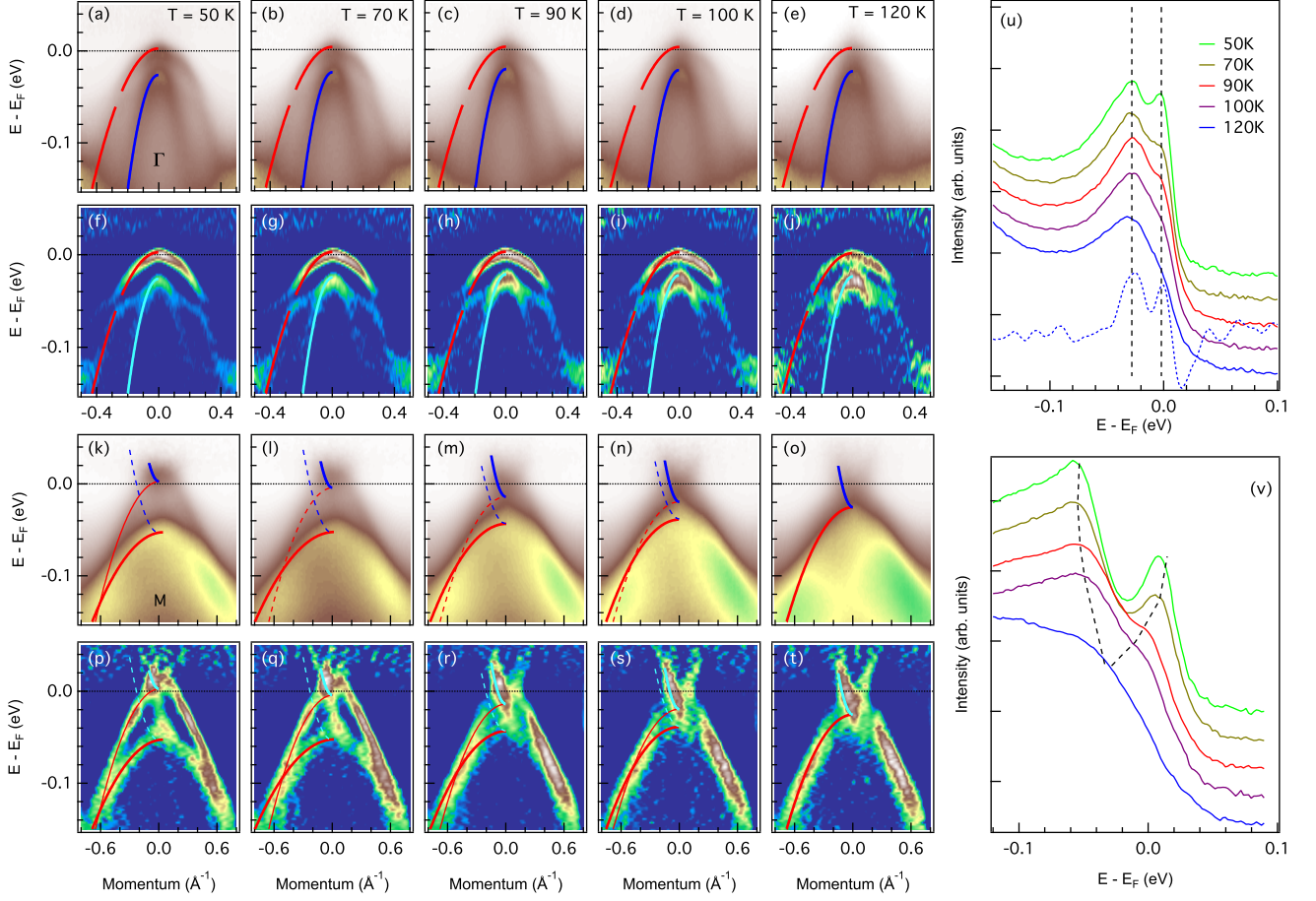


FIG. 2. (a - e) ARPES intensity plots of the band structure at Γ at different temperatures. The intensity in each plot is the sum of data acquired with C^+ and C^- polarized photons. (f - j) EDC curves of (a - e). (k - o) ARPES intensity plots of the band structure at the M point at different temperatures, recorded in the σ geometry. (p - t) MDC curves of (k - o). (u) EDCs of (a - e) at $k_x = 0$. The blue dashed line is the second derivative of the blue solid line with an extra minus sign. The two dashed black lines indicate the peak positions. (v) EDCs of (k - o) at $k_x = 0$. The black dashed lines correspond to the EDC peaks. In all the intensity plots, the red lines represent the d_{yz} orbitals, while the blue/cyan ones represent the d_{xz} orbitals. All cuts are along Γ -M or the Z-A high-symmetry direction. All the intensities are divided by Fermi function at the corresponding temperatures.

the order parameter responsible for the splitting at the M point must have an anisotropic form of orbital order, such as the d -wave orbital order defined on the Fe-Fe bonds [20]:

$$H_{bond} = \sum_{\mathbf{k}} \Delta_M(T) (\cos k_x - \cos k_y) (n_{xz}(\mathbf{k}) + n_{yz}(\mathbf{k})),$$

In Fig.3(d), we provide detailed calculations and show that the d -wave orbital order can explain the experimental band structure near the M point very well with an estimated coupling constant $\Delta_0 \sim 60$ meV in the low-temperature limit.

Two major candidates for the splitting at Γ /Z are the SOC [18] and the onsite ferro-orbital fluctuations [20]. However, both explanations contain severe flaws. Indeed,

SOC can break the glide symmetry that prevents the d_{xy} band at $k+Q$ to hybridize with the d_{xz}/d_{yz} bands at k in the 1-Fe unit cell (Supp. Part I) [24, 25]. However, such hybridization has an equal strength for both $d_{xy,\uparrow}/d_{xz,\downarrow}$ and $d_{xy,\uparrow}/d_{yz,\downarrow}$ hybridizations. Thus, the observation of hybridization between the d_{yz} and d_{xy} bands but not between the d_{yz} and d_{xz} bands is strongly against the SOC origin [26]. In addition, similar splitting at Γ has been reported to be strongly doping dependent in LiFeAs, which is apparently in contradiction with the SOC scenario [27]. The other candidate, the onsite ferro-orbital ordering or fluctuations, should remove the d_{xz}/d_{yz} degeneracy across the entire momentum space, as illustrated by our calculations shown in Fig.3(c), which is inconsistent with the absence of splitting at M above 120 K. Together with the doping-dependent splitting observed

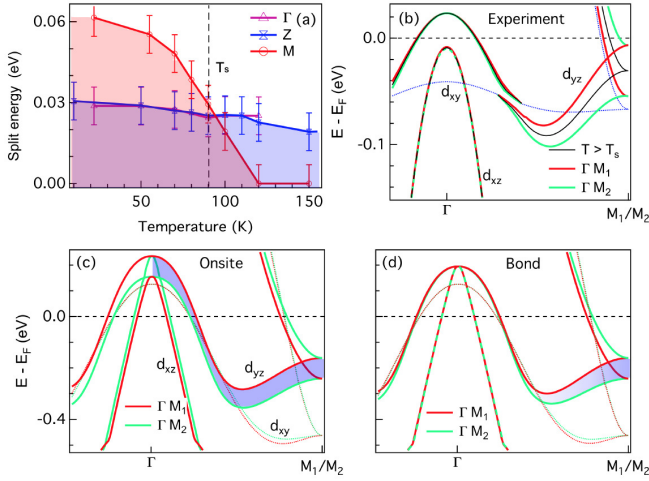


FIG. 3. (a) Summary of the d_{xz}/d_{yz} splittings at Γ , Z and M as a function of temperature. The splitting at M disappears at a slightly higher temperature than T_s , which might be caused by short-range ordering or fluctuations above the transition. (b) Draft of band structure extracted from experimental data and fitted with a tight binding model. The d_{xy} , d_{xz} and d_{yz} symbols are for $T > T_s$ only since the orbital characters will change along Γ -M₁ and Γ -M₂. (c - d) Band structure of onsite and bond orbital order, calculated from a tight binding model (see Supp. Part I for the details).

in LiFeAs [27], we have strong reasons to believe that in FeSe the splitting at Γ and the hybridization between the d_{xy} and d_{yz} bands originate from magnetic fluctuations. The magnetism in FeSe is more frustrated than in the iron-pnictides, and long-range magnetic ordering is thus unstable [28, 29]. However, nematicity and magnetic fluctuations can still be strongly coupled [30, 31]. Thus, the splitting at Γ and the hybridization between d_{xy} and d_{yz} observed above T_s are very likely signatures of this coupling. In any cases, our current results with two distinct d_{xz}/d_{yz} splittings suggest a more complicated interplay between the magnetic and orbital degrees in FeSe than previously expected.

In conclusion, we report the temperature evolution of the detailed electronic band structure in FeSe single-crystals. We observe two distinct d_{xz}/d_{yz} band splittings at the high-symmetry points. The splitting at M is related to the structural transition and has a d -wave form factor, while the splitting at Γ originates most likely from magnetic frustration. Our results clearly exclude the commonly-believed ferro-orbital order and require a new consideration of the origin and implication of the orbital order in FeSCs.

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